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**Grant no.:** N00014-99-1-0310

**Title:** Regenerative polymer membranes for water treatment applications

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**Organization:** Massachusetts Institute of Technology

## **Research Objectives and Approach**

Polymer membranes are an important and growing technology for water treatment applications such as desalination of sea and brackish water, water softening, production of ultrapure water, and purification of industrial, municipal and shipboard wastewater. Membrane processes offer significant advantages over conventional water treatment approaches, being inherently less energy intensive than distillation and more reliable than flocculation methods. However, membrane fouling remains a critical materials-related problem with this technology, causing reduced efficiency due to flux decline, high cleaning and maintenance costs, and low membrane lifetimes. Moreover, membrane selectivity and throughput are inherently limited by the inability to tailor pore microstructure in membranes fabricated by immersion precipitation methods.

To address these challenges, work supported under this grant explored surface segregation of amphiphilic comb polymer additives as an economical means to increase service lifetimes and enhance membrane function. In this approach, the surface-localized combs create a dense, foul-resistant layer of hydrophilic branches on all surfaces of the membrane. Advantages to this method include: 1) surface modification is accomplished *in situ* during the conventional membrane casting steps; 2) hydrophilic surface regions worn away by cleaning procedures can be regenerated by a simple thermal treatment; 3) porosity of the membrane separating layer is increased, resulting in higher pure water flux; and 4) added selectivity can be achieved by chemical modification of the comb side chains. To create the membranes, polymer blend compositions containing 5-20% comb additive were fabricated into membranes via standard immersion precipitation methods. Membranes were subsequently characterized for structure (pore morphology and comb surface coverage) and performance (e.g., fouling resistance, throughput, wettability, selectivity, and regenerative capability). To model the influence of process parameters on membrane morphology, a simulation tool based on lattice Boltzmann techniques was developed.

## **Research Highlights**

Immersion precipitated membranes with high flux and fouling resistance were prepared from blends of poly(vinylidene fluoride), PVDF, and a free-radically synthesized amphiphilic comb polymer having a methacrylate backbone and poly(ethylene oxide) side chains. X-ray

photoelectron spectroscopy (XPS) analysis indicated substantial surface segregation of the comb polymer during membrane coagulation took place, yielding an integrated near-surface coverage of up to 50 vol % comb for a membrane containing 10 wt % (14.6 vol %). Separation surface porosities for comb-modified membranes were found to be up to an order of magnitude higher than PVDF controls. With the combined benefits of fouling resistance and increased porosity, a membrane containing 10 wt % comb was over 20 times as permeable as a PVDF-only membrane with equivalent separation characteristics after 3 h of filtration of a foulant protein solution. The results demonstrate that surface segregation is a simple and effective method to membrane surface modification. A patent recently issued on this technology has been licensed by MIT to a major U.S. membrane manufacturer.

A significant effort under this grant was directed toward the synthesis of new amphiphilic graft copolymers for use as membrane surface modification agents. The direct preparation of amphiphilic graft copolymers from commercial poly(vinylidene fluoride) (PVDF) using atom transfer radical polymerization (ATRP) was achieved by direct initiation of the secondary fluorinated site of PVDF. Amphiphilic comb copolymer derivatives of PVDF having poly(methacrylic acid) side chains (PVDF-g-PMAA) and polyoxyethylene methacrylate side chains (PVDF-g-POEM) were prepared using this method. These materials were subsequently employed in the preparation of PVDF membrane prototypes. PVDF / 5 wt % PVDF-g-POEM membranes exhibited a near-surface POEM concentration of 42 wt %, wet spontaneously when placed in contact with water, and showed substantial resistance to BSA fouling.

Membranes comprising PVDF and PVDF-g-PMAA exhibited dramatic pH-responsive separation characteristics. XPS analysis indicated a near-surface coverage of ~60 wt % PVDF-g-PMAA on membranes containing 10 wt % comb. Fluorescence microscopy studies employing a cationic dye confirmed the surface expression of PMAA on internal pore channel surfaces throughout the membrane. In ultrafiltration studies, a reversible, pH-dependent flux variation of over an order of magnitude was observed as the feed solution pH is varied between 2 and 8. The pH-dependent conformational changes of the PMAA surface layer were further quantified via force spectroscopy in water. The findings demonstrate that "smart", environmentally responsive membranes can be prepared by immersion precipitation with no post-coagulation processing steps. A patent application has been filed on the ATRP synthesis method and resulting materials; the technology has been licensed to a major U.S. membrane manufacturer.

In an effort to prepare comb modifiers suitable for use in polysulfone (PSf) and polyethersulfone membranes, we have devised a novel synthetic route to graft copolymers having polysulfone backbones and polyethylene oxide (PEO) side chains that exploits Williamson Ether chemistry. In this approach, a base such as NaH or pyridine is reacted with polyethylene glycol monomethyl ether to form a nucleophile that can attack chloride groups on chlorinated polysulfone to create an ether bond, forming a PEO branch off the PSf backbone. Using this The method provides for graft polymers of well-controlled side chain molecular weight, and thus presents a significant advantage over conventional radical-based grafting methods (e.g., radiation treatments). A provisional patent application was recently submitted for this synthetic route and the resulting materials.

Further work under this grant was directed towards the development of a simulation tool to model the influence of processing parameters on membrane morphology. A lattice Boltzmann simulation for immiscible binary fluids was first developed which accounts for both diffusive and hydrodynamic modes, following the Shen and Chen (*Phys. Rev. E* **47**, 1993, 1815) method of forcing interactions. This mesoscale model was shown to correctly capture the classical phase separation mechanisms of nucleation and growth and spinodal decomposition under appropriate specified conditions. To simulate the immersion precipitation process, a third component was incorporated along with a modified boundary condition simulating solvent and nonsolvent interchange.

The simulation successfully predicts the asymmetric membrane morphology formed by the immersion precipitation process. We have exploited this simulation tool as a virtual laboratory to further investigate the effects of casting conditions on the cross-sectional membrane morphologies. Since membrane pore formation results from the interplay between two major hydrodynamic forces, namely diffusional driving forces vs. viscous drag forces, we have studied how these forces affect the membrane structure. Using the simulation, the influence of casting solution viscosity and polymer/coagulant compatibility on membrane morphology was explored. Increasing viscosity (i.e., the relaxation time parameter) causes a dramatic change in the cross-sectional morphology, particularly near the upper surface of the membrane. A more viscous casting solution results in a membrane with a thicker surface separating layer and increased propensity for finger formation. A decrease in compatibility between polymer and coagulant provides for faster phase separation dynamics, causing a morphological transition from compact, non-porous membranes to porous membranes of lower compaction. Simulation results are qualitatively consistent with experimental reports in the literature.

We have further performed experimental investigations aimed at understanding and controlling the morphology of pores in the top layer of membranes formed by immersion precipitation, as these pores control the separation characteristics of the membrane. In these experiments, the mass transfer kinetics were controlled by casting PVDF membranes at different temperatures and casting solution concentrations. Interconnected surface pore morphologies were observed by scanning electron microscopy for membranes cast at high concentration and/or temperature, supporting a mechanism of liquid-liquid demixing at the membrane surface by spinodal decomposition. The coarsening of this highly porous, interconnected morphology leads first to chain-like formations of discrete, noncircular pores and ultimately to scattered pores of circular shape and large size dispersity. Similar results for PSf membranes, which solidify via vitrification rather than crystallization, suggest a degree of universality in the mechanism of morphological development of asymmetric membrane surfaces. This new understanding of pore formation kinetics opens the possibility of tailoring membrane surfaces to achieve a high degree of porosity and pore size uniformity.